Magnetic optical scatterers and backaction
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To predict and explain the propagation of light through a medium, one particular quantity plays a major role: the mediums’ refractive index. As the first section of this chapter shows, its value, and how refractive index is spatially distributed is omnipresent in the explanation of a plethora of optical phenomena. How a refractive index comes about in natural materials is usually discussed in terms of the underlying response of the mediums’ constituent polarizable atoms to impinging electromagnetic waves. In the last decade, a new field of ‘metamaterials’ emerged, in which unconventional effective medium responses are generated by nanostructured ‘meta-atoms’. This thesis studies metamaterials in the near field through a quantity called ‘local density of optical states’ (LDOS). In the second section of this Chapter, we introduce the reader to the concept of the LDOS and its universal role in phenomena such as fluorophore emission and light scattering. Based on both concepts, we end by giving a motivation and outline of the topics covered within this thesis.
1.1 Refractive index

This thesis is set in a field of physics that is called ‘nanoscale-optics’. Optics is the branch of physics that deals with light, i.e., how light is emitted, how it propagates from A to B, and how it is absorbed. Optics, however, really is as much about matter as it is about light. Indeed, solutions of Maxwell’s equations in vacuum are simply unconfined plane waves that exhibit rectilinear propagation [1]. For useful phenomena to occur, such as reflection and refraction of rays in a lens, image formation in a camera, guiding of light in a telecommunications fiber, or the appearance of diffraction orders in a spectrometer, light must interact with polarizable matter. In particular, the material parameter that enters the problem is usually introduced in textbooks through the concept of refractive index [2]. To describe and predict the propagation of light one naturally follows the concept of rays traveling in straight lines from A to B, experiencing refraction as a ray traverses from one medium to the next. The key parameter describing the process, as formulated by Snellius in the 17th century is, in the simplest case, a single real-valued quantity: the refractive index \( n \equiv c/v \) defined as the ratio of the light’s speed in vacuum \( c \) and its speed in the medium \( v \) [3].

The concept of refractive index turns out to be an exceptionally powerful simplification of the processes taking place. In fact, electric and magnetic fields that are oscillating in time and space interact with large amounts of atoms, typically \( 10^{23} \) in a cm\(^3\) for a solid, that each have many degrees of freedom [4]. Yet the behavior of light is very well described by just one effective parameter for the medium, namely \( n \). Delving somewhat deeper into electrodynamics it turns out that it would be more appropriate to say that one deals with the effective medium parameters ‘dielectric permittivity’ \( \varepsilon \) and ‘magnetic permeability’ \( \mu \) [5]. To show the wealth of phenomena that the concept of effective medium parameter, or refractive index, explains, just consider that by lumping all the degrees of freedom of a material in one parameter, the making of layers, powders, fibers, etc. is sufficient to describe lensing, scattering, why clouds, paint and snow appear white, why one should buy polarizing sunglasses, the colorful reflection of opals and oil films, interference filters, etc. In fact, if one adapts the refractive index to be dispersive in frequency, or to be a tensorial quantity depending on propagation direction and polarization, one can extend its validity to deal with more complex materials such as metals and birefringent crystals [3].

The only two regimes where the effective medium approach is taken to break down is when either features in the material distribution become atomic in size, so that quantum confinement corrections set in [6], or when electric fields strengths are so large that nonlinear responses occur [7]. A range of interesting phenomena appear, such as harmonic generation, and
the optical Kerr effect which both are based on an intensity dependent refractive index. However, throughout this thesis, we will work in a regime where a material’s response to electromagnetic radiation depends linearly on the electromagnetic-field strengths. As a consequence, our chosen material parameters will not depend on the intensity of the light field. Furthermore, we note here that throughout this thesis light-matter interaction is treated in the classical (non-quantum) sense.

Microscopically, the overall response of a medium to electromagnetic radiation stems from the combined responses of the materials’ individual constituents, e.g., molecules of a gas or atoms of a solid dielectric described by their polarizability or electrons of a metal explained by a Drude model [8, 9]. For instance, the simplest textbook description of the permittivity of a crystalline insulating material would read

$$\varepsilon = 1 + \rho \alpha$$

(1.1)

where $\rho$ is the number density of atoms, and $\alpha$ is their polarizability, a number with units of volume, which quantifies how large a dipole moment is induced per unit strength of incident electric field. We refer to Jackson [1], Chapter 4 for further treatments of microscopic formulas to approximate $\varepsilon$. Based on this logical assumption, it is valid to ask when it is feasible to cover such an ‘effective’ response in a single quantity such as a refractive index. Surely, to be able to give a reasonable answer one has to assess and compare the characteristic length- and time-scales of the wave phenomenon of electromagnetic energy propagation to the characteristic values of the medium under investigation. In the optical regime, the typical wavelength of light is a $\mu$m, which is more than three orders of magnitude larger than the typical spacing of atoms in a crystal. It should be noted how in nature, at optical frequencies materials have an electric response $\varepsilon$, which could be either positive or negative, and no magnetic response, i.e., $\mu = 1$ as in vacuum. At this point it is interesting to summarize effective material parameter ranges available in nature in Fig. 1.1, a.

### 1.2 Effective media and metamaterials

Historically, there has been a large interest to extend the idea of an effective response also to nanostructured composites. In particular, suppose you create a mixed topology, such as by etching air holes in a solid material to obtain a nanoporous sponge, or when putting colloids in a liquid, then a logical question is how you estimate the refractive index of the mixture from that of the constituents. Since the separation of length scales is absent, an improved approach is required. Specifically, Bruggeman [10] and Maxwell-Garnett [11] have derived expressions for the effective refractive index of
mixtures of materials, for instance often used to predict the optical properties of powders and suspensions. For instance, the simplest effective medium theory would estimate the effective permittivity of a composite simply by averaging as

$$\varepsilon = \varepsilon_1 \phi + \varepsilon_2 (1 - \phi)$$  \hspace{1cm} (1.2)

where $\phi$ is the volume fraction of material of permittivity $\varepsilon_1$, with the remaining material having permittivity $\varepsilon_2$. This approach is equivalent to simply adding up the polarizabilities of constituents in vein of Eq. 1.1. Evidently, this would be a poor approximation for some topologies. For instance for a nanoporous metal film, you would expect a response that strongly depends on whether the metal forms a conductive percolating network or not, meaning that a dielectric host with metal inclusions would be very different from its inverted counterpart. Maxwell-Garnett’s formula

$$\varepsilon_{\text{eff}} = \varepsilon_m \frac{2(1 - \phi)\varepsilon_m + (1 + 2\phi)\varepsilon_i}{(2 + \phi)\varepsilon_m + (1 - \phi)\varepsilon_i}$$  \hspace{1cm} (1.3)

is an example of a mixing formula that treats isolated inclusions (volume fraction $\phi$, permittivity $\varepsilon_i$) very differently from the backbone $\varepsilon_m$. However,
note that since these are all averaging formulas, taking volume-fraction averages, these composites are always predicted to have $\varepsilon$ between those of the constituents, hence being constrained to the same range of refractive index values as achievable with unstructured materials.

In 1967, Veselago discussed the intriguing consequences of being able to utilize media with effective material parameters outside those available in nature [12]. Since the year 2000, many efforts have been devoted to make structures that appear to respond as if they are effective media with $\varepsilon$ and $\mu$ far from that of their constituents, in particular having $\mu$ different from one [13, 14, 15, 16, 17]. The central paradigm has been to generate so called meta-atoms that are subwavelength sized metallic resonators that have a resonant response that involves oscillating charge distributions (Fig. 1.1, b). If these oscillations include a circulating component, an effective magnetic dipole moment is set up. Most meta-atoms are hence loop-shaped particles with a gap that present an LC-resonance owing to the inductance of the loop and capacitance of the gap. The LC resonance means that each building block has a very large polarizability $\alpha$, compensating for the low density $\rho$ of objects. Moreover, the resonant response embodied in $\alpha$ can be both positive and negative, depending on how the driving frequency is chosen relative to the LC resonance frequency. Thereby, sizeable changes in permittivity and permeability can be achieved, with values outside the scope of traditional averaging formulas. In this way, optical magnetism was reported even at visible averaging wavelengths [18, 19, 20].

A key question is how valid the assignment of parameters $\varepsilon$ and $\mu$ is for structures accessible in experiment. Naturally, it is evident that a system with length scales exceeding the characteristic wavelength will diffract, and have grating orders. Thereby, it will not be ‘effective’. However, suppose a reflection/transmission measurement on a slab of material would tell us that it appears to be an effective medium. Are the same retrieved parameters then valid for all possible measurements, e.g., for incidence under any angle? This question has triggered a revisiting of theories of homogeneous media, in particular examining in how far the response of metamaterials can be captured as spatial dispersion in $\varepsilon$ [21]. And supposed that a metamaterials’ response in any far-field experiment can indeed be parametrized — through possibly tensorial effective dielectric and magnetic constants, in which experiments is it then discernibly not an effective medium. In particular, one expects that when one moves a probe to within a wavelength distance, comparable to the meta-atom size, effective medium parameters must break down. Exactly how this cross over occurs is highly interesting. The philosophy of this thesis is to address this question in the near field. As the key concept in this region, we will employ the local density of optical states which we introduce in following section.
1.3 Local density of optical states

Processes in nature which involve the conversion of the energy light ‘carries’ to change the state of an interacting piece of matter are manifold. One particularly relevant phenomenon is the process of photoluminescence \[22\]. An electron in the ground state of an atom, quantum dot, molecule, or impurity in a solid, might be promoted to an excited state in its energy level scheme, for instance by absorption of an incident photon or electrically as occurs in a LED. Relaxation to a lower-energy state via the re-emission of a photon can happen on different timescales depending on the probability of this high- to low-level electronic energy state transition to take place. A likely transition between two singlet states happens on the typical timescale of nanoseconds and is termed fluorescence. A much less likely spin forbidden transition from a triplet to a singlet state happens on timescales of milliseconds, and is termed phosphorescence. This difference in timescale indicates that the transition probability per unit of time depends on the excited state and final state electronic wave functions, and in particular on their overlap as embodied in the dipole matrix elements. It should be realized that the process of photon absorption can be considered as instantaneous as it is orders of magnitude faster (typically \(10^{-15}\) s) than the relaxation process.

The time scale of the relaxation process does not solely depend on the transition-dipole matrix elements of the involved electronic wave functions of the emitting object. The environment ‘into’ which the photon is released is of equal importance as transition probabilities incorporate not only the objects’ electronic level scheme, but also the available photonic states of the environment into which the photon can be released \[23\]. Transition rates for dipolar transitions from an initial state \(|i\rangle\) to a final state \(|f\rangle\) can be deduced from Fermi’s Golden Rule

\[
\gamma = \frac{2\pi}{\hbar^2} \left| \sum_{|f\rangle} \langle f | \hat{\mu} \cdot \hat{E} | i \rangle \right|^2 \delta(E_f - E_i) \tag{1.4}
\]

which sums matrix elements of the product of transition-dipole operator \(\hat{\mu}\) and radiation-field operator \(\hat{E}\) over all available final states under conservation of energy represented by the \(\delta\)-term. The final state \(|f\rangle\) encompasses the fate of both the fluorophore, ending up in a lower energy ground state, as well as the radiation field, now carrying an additional photon emitted from the fluorophore, after the transition process. All relevant information about the fluorophore is found within the electronic structure and wave function, i.e., the knowledge of excited and ground state energies separated by an energy difference of \(\hbar \omega\). However, the sum of Eq. 1.4 has to be carried out taking all available final states of the radiation field (with an additional photon of energy \(\hbar \omega\)) into account as well. Particularly in the context of
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so-called ‘photonic crystals’, a field developed in the late 1990’s and early 2000’s, it was realized that the availability of final states for the photon, as counted by \( \delta(E_f - E_i) \) can be strongly modified and even completely suppressed over large frequency bands \([24, 25, 26]\). Moreover, this availability of modes should not just count if a mode exists in the system (as embodied in the density of states), but also how strong each mode is at the location of a fluorophore. A canonical example is that of an emitter in a microcavity, where it is evident that coupling of the fluorophore to the cavity requires precise alignment with the cavity mode field maximum \([27, 28, 29, 30]\). This can be summarized by formulating the fluorescence transition rate as a quantity depending on transition-matrix elements \( \mu \) and a spatially dependent quantity called the local density of optical states (LDOS) \( \rho(r, \omega) \) fully characterizing the fluorophore’s environment \([23]\)

\[
\gamma = \frac{\pi \omega}{3 \hbar \varepsilon_0} |\mu|^2 \rho(r, \omega). \tag{1.5}
\]

The optical LDOS has been exploited in three ways. First, in particular photonic systems a controlled variation of LDOS \( \rho(r, \omega) \) can be generated, which allows to quantify the photophysics of an unknown fluorophore simply by varying its position in the LDOS landscape \([31, 32, 33, 34, 35, 36, 37]\). Second, if one has known fluorophores one can use them to map the LDOS of an unknown photonic system by measuring decay rate as a function of \( r \) and \( \omega \) \([38, 39, 40, 41]\). Third, for the fabrication of efficient single-photon sources and quantum-optics devices, there is a large demand for controlled engineering of \( \rho(r, \omega) \) in order to ensure that an emitter couples selectively to a given mode, in order to completely control how fast a photon is emitted after excitation, and in order to reach strong light-matter interaction \([42]\). We will now review the first two of these three uses.

Monitoring the influence of a non-uniform environment on the fluorescence behavior of an emitter allows one to calibrate the emitters’ fluorescence properties. Indeed, a common question when desiring to quantify an unknown fluorophore is what its quantum efficiency and oscillator strength (embodied in \( \mu \)) is. A non-unity quantum yield comes about when the excited state has a nonradiative decay channel (decay rate \( \gamma_{\text{nonrad}} \)) in addition to the radiative decay, for instance due to the generation of phonons, i.e., heat. Since the nonradiative decay does not involve a photon it has a rate independent of the photonic mode structure, meaning that the total fluorescence decay rate one would measure in a fluorescence decay-rate measurement that maps intensity \( I(t) = I_0 \exp(-\gamma t) \) is

\[
\gamma = \gamma_{\text{nonrad}} + \rho(r, \omega)\gamma_{\text{rad}}. \tag{1.6}
\]

The first experimental realization of this approach by Drexhage et al. \([43]\) studied the fluorescence lifetime of europium ions as a function of the dis-
tance to a silver mirror and showed that solely the radiative decay rate of
the emitter was affected by the environment, leaving the nonradiative de-
cay rate unchanged. Knowledge of both decay rates allows for quantita-
tive assessment of the fluorescence process in the form of an intrinsic quantum
efficiency. This approach lent the name to a plethora of Drexhage-type ex-
periments and the study of fluorophores [31, 32, 33], quantum dots [34],
nitrogen vacancy centers [35, 36] in diamond and magnetic dipole transi-
tions [37]. Figure 1.2 shows the decay rate enhancement $\Gamma$ compared to
vacuum LDOS for a dipole oriented perpendicular and parallel to a perfect
mirror ($\varepsilon = -\infty$).

Furthermore, the same qualitative effect of the environment’s LDOS is
found in the scattering properties of plasmonic particles (introduced in the
previous section). If one has a plasmonic scatterer of sufficient size (radius
above 20 nm), it is a resonant polarizable object that has as dominant loss
channel radiation of its excitation as scattered light into the far field. Since
the LDOS modifies the number of channels available to radiate into, one
expects that the radiation damping of a scatterer varies as a function of
LDOS. Indeed Buchler et al. [44] showed that a plasmonic particle’s extinc-
tion cross section linewidth plotted as a function of particle-mirror distance
follows an LDOS lineshape. This effect of a mirror on the scattering prop-
erties of a plasmon particle can be viewed as a backaction, whereby the
particle is not only driven by an incident field, but also by its own mirror
image. This backaction essentially renormalizes the particle’s polarizability
tensor. In contrast to the transition-dipole picture in the fluorophore case,
here, the radiation of externally driven dipole(s) (spatial charge separation
in the classical sense) is affected by the presence of a mirror, again allowing
for characterization of the radiating dipole(s) quantum efficiency and the
particle’s plasmon spectrum.

Turning to the second exploitation of LDOS, once one has full knowledge
of the behavior of an emitter embedded in a homogeneous reference medium
(for simplicity: vacuum) allows one to use this characterized emitter as a
reference probe. Bringing such an emitter in proximity to an unknown, pos-
sibly inhomogeneous and therefore more intricate structure, one can map
the LDOS in the structures’ surrounding. Examples range from the study of
plasmonic nanowires with scanning tips featuring fluorescent molecules [38]
or nitrogen vacancy centers [39] to the complete mapping of photonic crys-
tals with quantum dots [40] and mode structure analysis of photonic cavities
by cathodoluminescence spectroscopy [41].
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Figure 1.2: A radiating dipole separated from a perfect mirror ($\varepsilon = -\infty$) at a geometrical distance $d$ will experience a decay rate enhancement $\Gamma$ (compared to the dipole in vacuum) depending on the dipole orientation. We plot $\Gamma$ for two particular dipole orientations with distances presented in units of wavenumber $\times$ distance: $kd$. A dipole oriented parallel to the mirror surface experiences a total inhibition of its radiative decay when touching the mirror surface (black). In contrast, a dipole oriented perpendicular to the mirror surface experiences a decay rate enhancement of factor 2 when being brought close to the surface (gray). For ever larger distances, the decay rate will not be affected by the mirror and will reach the value for vacuum, independent of the dipole orientation.
1.4 Motivation and thesis outline

Having given a very brief introduction into first, the field of effective media and the realization of artificial metamaterials based on resonant plasmonic building blocks and second, the concept of the local density of optical states in the context of the fluorescence phenomenon, we want to state our motivation. The philosophy of the PhD research project presented in this thesis was to obtain a better understanding of what a metamaterial, and what a metamaterial scatterer is, through LDOS. In particular, at the time this research was initiated, far-field normal-incidence transmission spectra measured on 2D arrays of split-ring scatterers were reported and interpreted as implying effective medium behavior with negative $\varepsilon$ and $\mu$ [20, 21, 45, 46]. This behavior was attributed to individual building blocks, i.e., the split rings, and the notion that these are subwavelength polarizable dipoles with a coupled electric and magnetic response [19, 20, 47, 48, 49]. From these assertions the following questions emerge:

1. What should the LDOS for a dipole with an electric-dipole allowed transition actually be if one would have a hypothetical magnetic mirror or magnetic and electric metasurface (Fig. 1.3, a)?
2. Up to what point are effective $\varepsilon$ and $\mu$ derived from far-field normal-incidence data actually good descriptors for a metamaterial, as one brings a probe from the far field into the near field to measure LDOS?
3. Can we strengthen or refute the claim that a single split ring is a magnetic dipole scatterer by probing if its radiation damping actually traces out magnetic LDOS (Fig. 1.3, b)?
4. How do single building-block magnetism on one hand, and packing of objects in 2D periodic arrays on the other hand that must have collective Bloch modes conspire to give magnetic signatures in LDOS, and in far-field observables?

Since proposed metamaterial applications are mainly near-field applications, i.e., perfect lensing, cloaking, and transformation optics, experiments towards answering these four questions force one to come much closer to understanding metamaterials than far-field transmission and reflection experiments alone [50, 51, 52, 53, 54, 55].

In this thesis, we report on research intended to provide answers to the four key questions posed above. A first prerequisite to probe LDOS near surfaces is to establish a method to controllably separate LDOS probes and the surfaces that provide the LDOS change. An effective way of realizing a structure fulfilling the requirements of controlled distances on the
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![Figure 1.3: Questions raised and addressed within this thesis include: (a) What is the LDOS at the position of a radiating (transition) dipole above a metasurface? (b) How does the presence of a mirror affect the scattering properties of a magneto-electric scatterer such as a SRR?](image)

nanometer scale over a large sample area on the micrometer scale is presented in Chapter 2. We show how, by applying gray-tone UV-lithography, a wedge-shaped dielectric can serve as a spacer layer between a silver mirror and a layer of fluorophores (dyes, quantum dots). Covering a range of distances up to about the respective fluorophores' emission wavelength, we effectively implement Drexhage’s method to conduct quantitative decay rate measurements on emitter ensembles and can calibrate and compare intrinsic quantum efficiencies.

In Chapter 3, we discuss the concept of introducing a magneto-electric scatterer such as a split ring resonator (SRR) into a photonic environment with a well-known density of optical states such as a mirror. We predict that the scatterer’s extinction cross-section linewidth depends on its distance to the mirror-surface due to a combination of electric, and magnetic local density of states effect, in accordance with earlier claims that split rings have both an electric and a magnetic dipole contribution to their scattering. Moreover, split rings have been predicted to have nonzero cross-coupling, meaning that electric fields can drive magnetic responses and vice versa. This effect is coined ‘bi-anisotropy’, and is strongly related to chiral responses of scatterers. Strikingly, the non-zero cross-coupling components in the scatterer’s polarizability tensor will be reflected in the extinction cross-section lineshape. For a SRR, this lineshape differs from a lineshape expected from a purely electric or magnetic dipole. We show how this difference is stemming from the interplay of both dipole components as predicted by our analytical magneto-electric point-dipole model and support our finding by finite-element simulation.
Chapter 4 covers periodic two-dimensional arrangements of split ring resonators. We compare two types of lattices, indistinguishable by the individual split ring orientation within their respective unit cell. Transmission measurements conducted on (i) diffractive and (ii) nondiffractive realizations of both types of lattices reveal (i) the background-free signature of magnetic dipole response in Fourier imaging on illumination on resonance and (ii) a reduction of the apparent bi-anisotropy effect for off-normal illumination. A general model for metamaterial lattices with complex 2D unit cell of poly-atomic basis is introduced and explains experimentally observed phenomena. Furthermore, we extend this model to treat finite stacks of 2D lattices and calculate reflection and transmission spectra as a function of the number of layers. This model provides all the essential ingredients required to predict the LDOS change that metasurfaces will induce.

We combine our experience of sub-100 nm distance control and our comprehension of metasurfaces in Chapter 5 by studying combined systems of lattices formed by periodic arrangements of magneto-electric scatterers in front of a mirror. Combining the lattice-sum formalism with the interface Green-function approach we analytically calculate the renormalization of the per-particle polarizability and extract reflection coefficients. Calculated reflection and transmission coefficients for the individual interfaces serve as input parameters in a simple Fabry-Pérot model and apparent differences to the analytical approach are discussed that are interpreted in terms of back-action. A system comprised of SRR lattices separated from a silver mirror by a dielectric wedge spacer is fabricated and reflectivity data is acquired as a function of separation and frequency for different pitches. The experimentally acquired distance dependent reflectivity is compared to predictions of our lattice-sum magnetoelectric point-dipole model. Both find clear discrepancies to a simple Fabry-Pérot model which neglects the near-field influence on the single lattice atom’s polarizability.
1.5 References


References


